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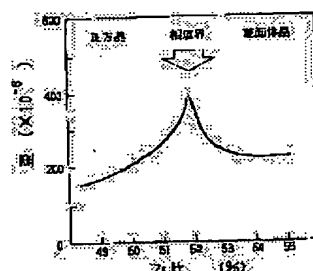
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## (54) FERROELECTRIC CERAMIC COMPOSITION

### (57)Abstract:

**PURPOSE:** To provide a composition which uses a tetragonal system, is kept in good proportion to a strong electric field to cause large distortion, is not much affected by the temperature change of atmosphere and is excellent in durability.

**CONSTITUTION:** A ferroelectric ceramic composition is obtained by addition of SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, SrO or BaO, etc., to PZT or a PZT system substance. Its crystal system is tetragonal wherein Zr ratio expressed as Zr/(Zr+Ti) is set to be at least 0.5mol% smaller than that of a phase boundary.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The ferroelectric porcelain constituent which it comes to add additives, such as SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and SrO, BaO, to a PZT or PZT system, and the crystal system is made into tetragonal system, and is characterized by setting up Zr ratio expressed with  $Zr/(Zr+Ti)$  smaller at least 0.5 mole percents than Zr ratio of a phase boundary.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the amelioration technique of the ferroelectric porcelain constituent represented by electrostrictive ceramics.

[0002]

[Description of the Prior Art] When a strong electrical potential difference is impressed, the ferroelectric porcelain constituent (it abbreviates to a "ferroelectric" hereafter.) is adopted as mechanical components (actuator), such as a minute positioning device, using the property (inverse piezoelectric effect) in which a ferroelectric carries out distorted deformation.

[0003]

[Problem(s) to be Solved by the Invention] The above-mentioned ferroelectric takes the value of the phase boundary where the property at the time of generally the electrical potential difference of 1V (bolt) extent being impressed is made the best, and is application-ized.

[0004] However, the ferroelectric selected on the basis of the property near a phase boundary tends to be influenced of ambient temperature, and needs to perform suitable temperature compensation.

[0005] moreover, distorted as an actuator — it is so good that a variation rate is large, and although he wants to raise applied voltage to 1kV for the reason, when such a high voltage is impressed, the conventional thing keeps that it is poor and there is no \*\*\*\* in practical use.

[0006] Then, the purpose of this invention is to offer the ferroelectric which combines the electric-field property of bearing the high voltage, endurance, and the good temperature characteristic.

[0007]

[Means for Solving the Problem and its Function] That the above-mentioned purpose should be attained, in a ferroelectric porcelain constituent, additives, such as  $\text{SnO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{SrO}$ ,  $\text{BaO}$ , are added to a PZT or PZT system, it becomes it, the crystal system is made into tetragonal system at it, and this invention is characterized by Zr ratio expressed with  $\text{Zr}/(\text{Zr}+\text{Ti})$  being smaller than Zr ratio of a phase boundary at least 0.5 mole percents, and being set up.

[0008]

[Example] The result studied wholeheartedly that this invention person should improve the fault of the conventional PZT system ferroelectric, Are what added  $\text{Nb}_2\text{O}_5$  of a minute amount, and  $\text{SnO}_2$  to the PZT system ferroelectric, and the ferroelectric of tetragonal system has a good electric-field property and endurance. And it is as finding out that the extremely characteristic ferroelectric porcelain constituent which is not looked at by the former that it cannot be easily influenced by the environmental temperature change is obtained, reaching this invention, and describing the detailed contents below. In addition, PZT is the abbreviated name of  $\text{Pb}(\text{Zr}, \text{Ti}) \text{O}_3$  crystalline.

[0009] Drawing 1 is the related Fig. of Zr ratio and a lattice constant in the ferroelectric containing the ferroelectric concerning this invention, manufactures two or more kinds of samples to which the Zr ratio was changed by the process of the usual electrostrictive ceramics centering on the constituent which added slight  $\text{Nb}_2\text{O}_5$  and  $\text{SnO}_2$  to PZT, and asks these for a lattice constant by powder X-ray diffraction.

[0010] In addition, the above-mentioned Zr ratio is expressed with  $\text{Zr}/(\text{Zr}+\text{Ti})$ , and means the mole fraction of Zr contained in a constituent. On a notation, this is doubled 100 and it expresses with mole percent.

[0011] In drawing 1, it is  $c = 4.113$ ,  $a = 4.049\text{\AA}$ , and axial ratio ( $c/a$ ) = 1.0158 in the Zr ratio 49.0, and it turned out that a c-axis is small, an a-axis becomes large, an axial ratio ( $c/a$ ) approaches 1.0, and the phase boundary which phase transition produces [ Zr ratio ] from \*\*\*\*\* to \*\*\*\*\* in the 52.0 to 52.25 neighborhood exists in an increment and \*\* of Zr ratio. It turned out that this to Zr ratio is tetragonal system or less in 52, and Zr ratio is a rhombohedral system or more in 52.25.

[0012] It carries out grinding of said sample to 1mm in thickness, drawing 2 is drawing showing Zr ratio of the ferroelectric containing the ferroelectric concerning this invention, and distorted relation, after it is able to be burned in a silver paste electrode, it impresses the electrical potential difference of 700V, and it shows what measured distortion using the non-contact type laser displacement gage and the strain gage.

[0013] As for distortion, according to drawing 2, Zr ratio serves as max near 52.0–52.25. This is considered to be the presentation which the constituent near a phase boundary is soft and is easy to be distorted. And that the constituent near a phase boundary was adopted conventionally originates in distortion being large.

[0014] Drawing 3 (a) – (c) is drawing showing change of d constant when applying an electrical potential difference in the ferroelectric containing the ferroelectric concerning this invention, impresses the direct current voltage to 1.2kV/mm to the sample by which grinding was carried out to 1mm in said thickness, and plots piezo-electric d constant (it abbreviates to "d constant" hereafter.) computed based on distortion of 31 directions generated on this occasion.

[0015] Zr ratio can set drawing 3 (a) in the sample of 49.0–51.75, i.e., tetragonal system, d constant becomes large, so that Zr ratio is large, and as for d constant, 51.0 or less thing is mostly in direct proportion to the magnitude of electric field for Zr ratio. However, Zr ratio is decreasing with a peak of near 1kV/mm about 51.75.

[0016] drawing 3 (b) — Zr ratio — 52. — to the sample 0 and 52.25, i.e., near a phase boundary, although d constant is large, it is decreasing from near 0.7kV/mm.

[0017] drawing 3 (c) — Zr ratio — 53. — to the sample of 0 and 55.0, i.e., a rhombohedral system, while d constant is small, it cannot be said that it is in an increment and proportionality of electric field.

[0018] Drawing 3 (a) In order to obtain d constant which comparatively big d constant was obtained so

that - (c) might show, and is proportional to field strength, it is tetragonal system and Zr ratio can say that the sample of the 51.0 neighborhoods is desirable.

[0019] Drawing 4 is drawing showing the temperature effect nature of the ferroelectric containing the ferroelectric concerning this invention, and an axis of ordinate is a distortion rate in 60 degrees C when setting 0 degree C to 1.0, and increases rapidly to 1.2 or more times with a phase boundary and a rhombohedral system to a distortion rate being about 1.13 in tetragonal system. It is shown to change of ambient temperature that the sample of tetragonal system is the hardest to be influenced.

[0020] Drawing 5 is drawing showing the distorted rate of change by the electrical-potential-difference repetition durability test of the ferroelectric containing the ferroelectric concerning this invention, in the direct-current bias of 1.2 VK/mm and 1HZ, the distorted rate of change 1000 times, 10000 times, and after impressing 75000 times is shown, degradation progresses and a rhombohedral system is also accepted for degradation on a phase boundary.

[0021] On the other hand, extent of degradation [ in tetragonal system ] also after 75000 times is very small, and its endurance is large.

[0022] the ferroelectric porcelain constituent suitable from the above thing for an actuator — tetragonal system — and at least 0.5 mole percents from Zr ratio of a phase boundary — small — what was set as \*\*\*\* Zr ratio is suitable.

[0023] In addition, it is desirable that Zr ratio is set as the range of 50.0-51.50 in the example shown in drawing 3 (a) - (c) since generating distortion became small as it was shown in drawing 2 and drawing 3 (c), when each property tended to become unstable when a setup of Zr ratio was too close to the phase boundary, and a setup of Zr ratio was too small, and there was no \*\*\*\* in practical use.

[0024] In addition, the additive for a PZT system is good also as oxides, such as Nb<sub>2</sub>O<sub>5</sub> and not only SnO<sub>2</sub> but SrO, BaO, etc. Moreover, as for the ferroelectric of this invention, it is needless to say that it may be used as a ferroelectric of not only electrostrictive ceramics but a wide sense.

[0025]

[Effect of the Invention] Since the ferroelectric porcelain constituent of this invention is tetragonal system, it maintains good proportionality to strong electric field, produces a big distortion, and it is seldom influenced by the temperature change of an ambient atmosphere, and its endurance is good as stated above. Therefore, according to this invention, a reliable ferroelectric porcelain constituent can be offered by high power.

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#### DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The related Fig. of Zr ratio and a lattice constant in the ferroelectric containing the ferroelectric concerning this invention

[Drawing 2] Drawing showing Zr ratio of the ferroelectric containing the ferroelectric concerning this invention, and distorted relation

[Drawing 3] Drawing showing change of d constant when applying an electrical potential difference in the ferroelectric containing the ferroelectric concerning this invention

[Drawing 4] Drawing showing the temperature effect nature of the ferroelectric containing the ferroelectric concerning this invention

[Drawing 5] Drawing showing the distorted rate of change by the electrical-potential-difference repetition durability test of the ferroelectric containing the ferroelectric concerning this invention

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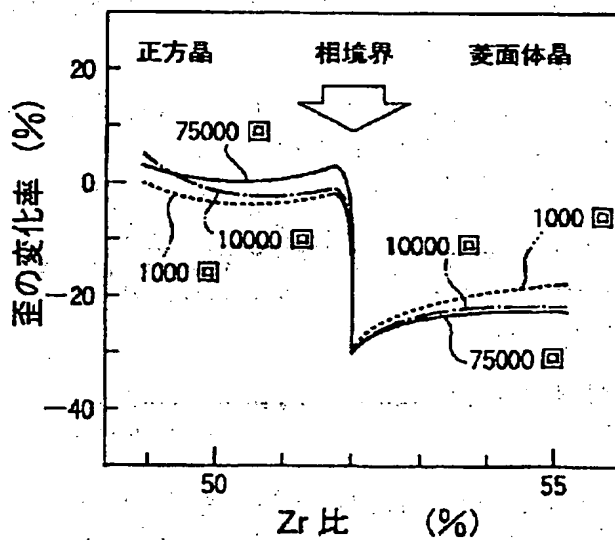
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(54)【発明の名称】 強誘電体磁器組成物

(57)【要約】

【構成】 PZTまたはPZT系に $\text{SnO}_2$ , Nb $_2\text{O}_5$ , SrO, BaO等の添加物を加えてなり、その結晶系が正方晶系とされ、 $\text{Zr}/(\text{Zr}+\text{Ti})$ で表わされるZr比が相境界のZr比より少なくとも0.5モルパーセント小さく設定されたことを特徴とする強誘電体磁器組成物。

【効果】 本発明の強誘電体磁器組成物は、正方晶系なので強電界に対し良好な比例関係を保って大きな歪を生じ、雰囲気温度変化にもあまり影響されず、且つ、耐久性良好である。



## 【特許請求の範囲】

【請求項1】 P Z TまたはP Z T系に $\text{SnO}_2$ 、 $\text{Nb}_2\text{O}_5$ 、 $\text{SrO}$ 、 $\text{BaO}$ 等の添加物を加えてなり、その結晶系が正方晶系とされ、 $Z_r / (Z_r + T_i)$ で表わされる $Z_r$ 比が相境界の $Z_r$ 比より少なくとも0.5モルパーセント小さく設定されたことを特徴とする強誘電体磁器組成物。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は圧電セラミックスに代表される強誘電体磁器組成物の改良技術に関する。

## 【0002】

【従来の技術】強い電圧を印加した時に強誘電体が歪変形する性質（逆圧電効果）を利用して微小位置決め装置等の駆動部（アクチュエータ）に強誘電体磁器組成物（以下、「強誘電体」と略す。）が採用されている。

## 【0003】

【発明が解決しようとする課題】上記強誘電体は、一般に1V（ボルト）程度の電圧が印加された際の、特性が最も良いとされている相境界の値をとって応用化されている。

【0004】しかし、相境界付近の特性を基準に選定された強誘電体は、周囲温度の影響を受けやすく、適当な温度補正を施す必要がある。

【0005】又、アクチュエータとしては、歪変位が大きい程良く、その為に印加電圧を例えば1KVにアップしたいが、従来のものはこのような高電圧を印加するとへたってしまい実用に供さない。

【0006】そこで本発明の目的は、高電圧に堪える電界特性と、耐久性と、良い温度特性とを兼ね備えた強誘電体を提供することにある。

## 【0007】

【課題を解決するための手段及び作用】上記目的を達成すべく本発明は、強誘電体磁器組成物をP Z TまたはP Z T系に $\text{SnO}_2$ 、 $\text{Nb}_2\text{O}_5$ 、 $\text{SrO}$ 、 $\text{BaO}$ 等の添加物を加えてなり、その結晶系が正方晶系とされ、 $Z_r / (Z_r + T_i)$ で表わされる $Z_r$ 比が相境界の $Z_r$ 比より少なくとも0.5モルパーセント小さく設定されたことを特徴とする。

## 【0008】

【実施例】本発明者は、従来のP Z T系強誘電体の欠点を改良すべく鋭意研究した結果、P Z T系強誘電体に微量の $\text{Nb}_2\text{O}_5$ 、 $\text{SnO}_2$ を添加したもので且つ正方晶系の強誘電体は良好な電界特性及び耐久性を有し、且つ環境の温度変化に影響され難いという従来に見られない極めて特徴のある強誘電体磁器組成物が得られることを見出し本発明に到達したものであり、その詳しい内容は以下に述べる通りである。なお、P Z Tは $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ 結晶体の略称である。

【0009】図1は本発明に係る強誘電体を含む強誘電

体における $Z_r$ 比と格子定数の関係図であり、P Z Tに僅かな $\text{Nb}_2\text{O}_5$ 、 $\text{SnO}_2$ を加えた組成物を中心に、その $Z_r$ 比を変化させたところの複数種類の試料を通常の圧電セラミックスの製法で製造し、これらを粉末X線回析により、格子定数を求めたものである。

【0010】なお、上記 $Z_r$ 比は $Z_r / (Z_r + T_i)$ で表わされ、組成物中に含まれる $Z_r$ のモル分率を意味する。表記上、これを100倍してモルパーセントで表わす。

【0011】図1において、 $Z_r$ 比49.0で $c = 4.113$ 、 $a = 4.049$ オングストローム、軸比 $(c/a) = 1.0158$ であり、 $Z_r$ 比の増加と共に、 $c$ 軸は小さく、 $a$ 軸は大きくなり、軸比 $(c/a)$ が1.0に近づき、 $Z_r$ 比が52.0～52.25付近で正方晶から菱面体晶へ相転移が生じる相境界が存在していることが分かった。このことから $Z_r$ 比が52以下では正方晶系であり、 $Z_r$ 比が52.25以上では菱面体晶系であることが分かった。

【0012】図2は本発明に係る強誘電体を含む強誘電体の $Z_r$ 比と歪の関係を示す図であり、前記試料を厚さ1mmに研削し、銀ペースト電極を焼き付けた後に700Vの電圧を印加し、非接触式レーザ変位計及び歪ゲージを用いて歪を測定したものを示す。

【0013】図2によれば、 $Z_r$ 比が52.0～52.25の付近で歪は最大となる。これは相境界付近の組成物が軟かくて歪易い組成であると考えられる。そして、従来、相境界付近の組成物が採用されていたのは、歪が大きいことに起因している。

【0014】図3(a)～(c)は本発明に係る強誘電体を含む強誘電体に電圧を掛けた時の $d$ 定数の変化を示す図であり、前記厚さ1mmに研削された試料に1.2KV/mmまでの直流電圧を印加し、この際に発生した31方向の歪に基づいて算出した圧電 $d$ 定数（以下、「 $d$ 定数」と略す。）をプロットしたものである。

【0015】図3(a)は $Z_r$ 比が49.0～51.75、即ち正方晶系の試料におけるものであり、 $Z_r$ 比が大きい程 $d$ 定数が大きくなり、 $Z_r$ 比が51.0以下のものは電界の大きさに $d$ 定数はほぼ正比例している。しかし、 $Z_r$ 比が51.75については1KV/mm付近をピークに減少傾向にある。

【0016】図3(b)は $Z_r$ 比が52.0、52.25、即ち相境界付近の試料に対するもので、 $d$ 定数は大きいものの、0.7KV/mm付近から減少傾向にある。

【0017】図3(c)は $Z_r$ 比が53.0、55.0、即ち菱面体晶系の試料に対するもので、 $d$ 定数が小さいとともに電界の増加と比例関係にあるとは言えない。

【0018】図3(a)～(c)から分かるように比較的大きな $d$ 定数が得られ、且つ電界の強さに比例した $d$

定数を得るためには、正方晶系で且つ、Zr比が51.0付近の試料が好ましいと言える。

【0019】図4は本発明に係る強誘電体を含む強誘電体の温度影響性を示す図であり、縦軸は0℃を1.0としたときの60℃における歪率であり、正方晶系では歪率が約1.13であるのに対し、相境界及び菱面体晶系では1.2倍以上に急増する。雰囲気温度の変化に対し、正方晶系の試料が最も影響され難いことを示す。

【0020】図5は本発明に係る強誘電体を含む強誘電体の電圧繰返し耐久試験による歪の変化率を示す図であり、1.2VK/mm, 1HZの直流バイアスを1000回、10000回及び75000回印加した後の歪の変化率を示すもので、相境界では劣化が進み、菱面体晶系も劣化が認められる。

【0021】一方、正方晶系では75000回後でも劣化の程度は微少であり、耐久性が大きい。

【0022】以上のことから、アクチュエータに好適な強誘電体磁器組成物は正方晶系で且つ相境界のZr比から少なくとも0.5モルパーセント小さなZr比に設定したものが好適である。

【0023】なお、Zr比の設定が相境界に近すぎると各特性が不安定になりやすく、又、Zr比の設定が小さすぎると図2、図3(c)に示した通り発生歪が小さくなり、実用に供さないもので、図3(a)～(c)に示し

た実施例においてはZr比は50.0～51.50の範囲に設定されることが好ましい。

【0024】なお、PZT系の為の添加物は $\text{Nb}_2\text{O}_5$ ,  $\text{SnO}_2$ に限らず $\text{SrO}$ ,  $\text{BaO}$ 等の酸化物としてもよい。又、本発明の強誘電体は圧電セラミックスに限らず広義の強誘電体として使用され得ることは勿論である。

【0025】

【発明の効果】以上に述べた通り本発明の強誘電体磁器組成物は、正方晶系なので強電界に対し良好な比例関係を保って大きな歪を生じ、雰囲気温度変化にもあまり影響されず、且つ、耐久性良好である。よって、本発明によれば高出力で信頼性の高い強誘電体磁器組成物が提供できる。

【図面の簡単な説明】

【図1】本発明に係る強誘電体を含む強誘電体におけるZr比と格子定数の関係図

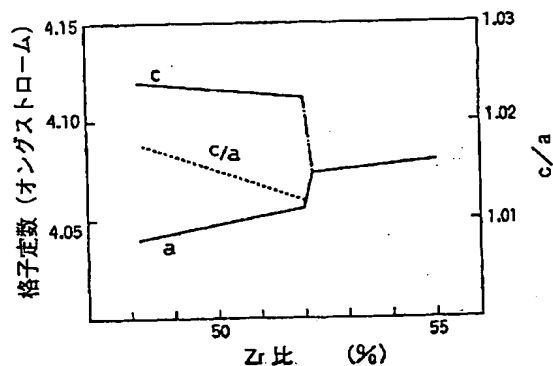
【図2】本発明に係る強誘電体を含む強誘電体のZr比と歪の関係を示す図

【図3】本発明に係る強誘電体を含む強誘電体に電圧を掛けた時のd定数の変化を示す図

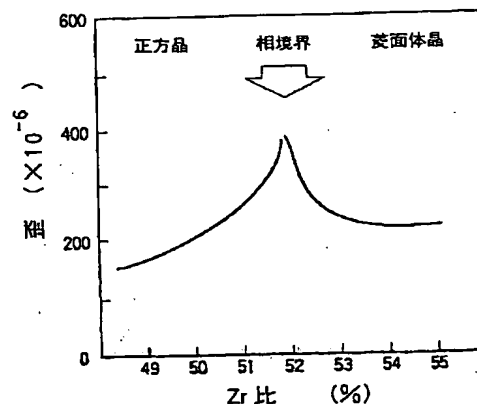
【図4】本発明に係る強誘電体を含む強誘電体の温度影響性を示す図

【図5】本発明に係る強誘電体を含む強誘電体の電圧繰返し耐久試験による歪の変化率を示す図

【図1】

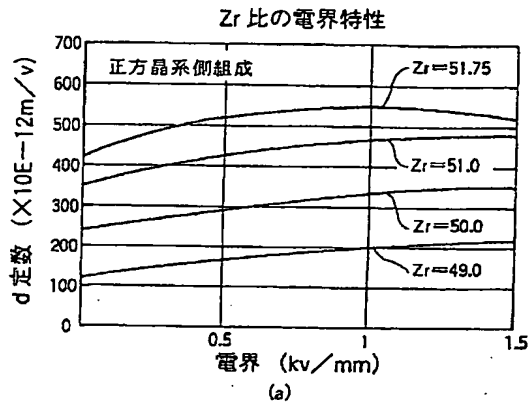


【図2】

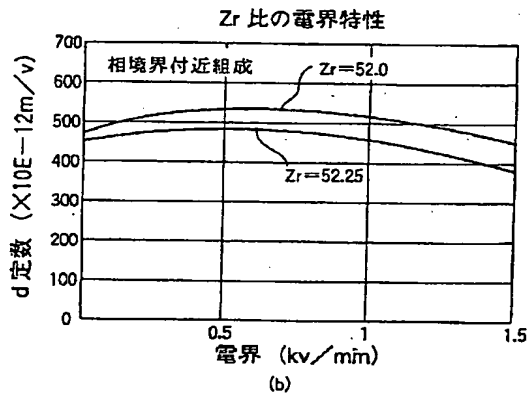
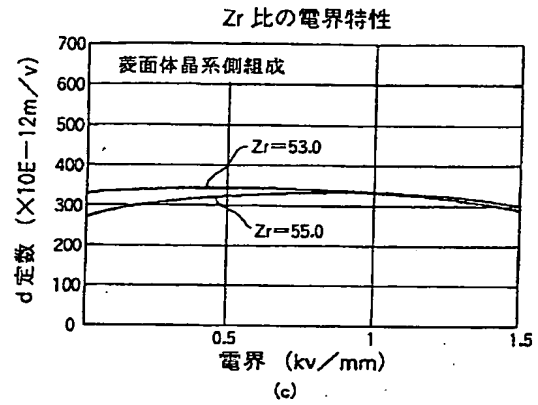




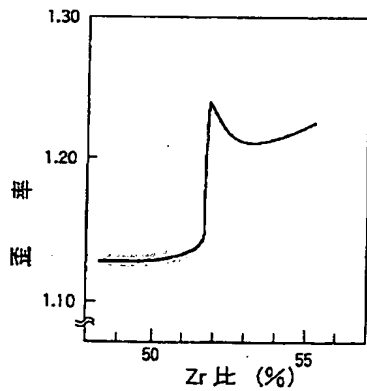
【図3】



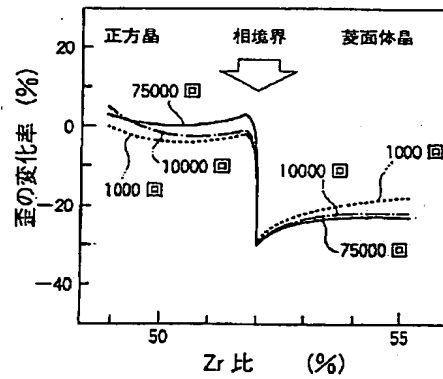
【図3】



【図4】



【図5】



【手続補正書】

【提出日】平成5年5月28日

【手続補正1】

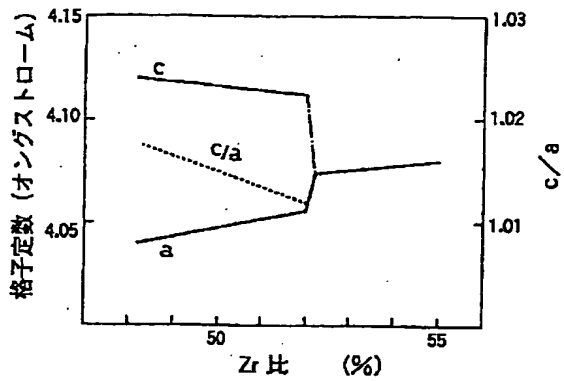
【補正対象書類名】図面

【補正対象項目名】全図

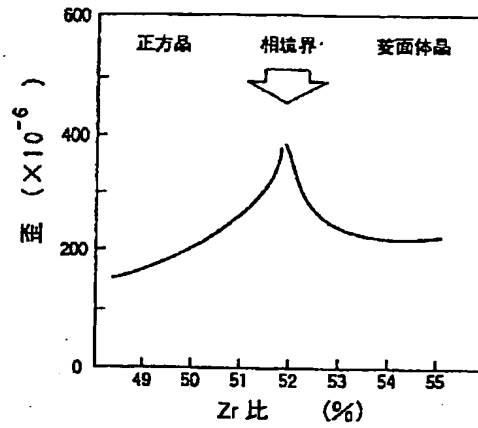
【補正方法】変更

【補正内容】

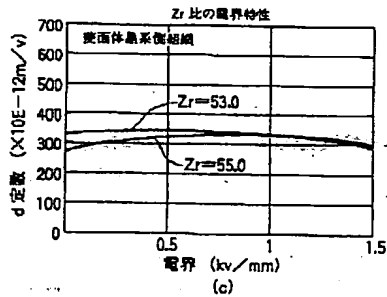
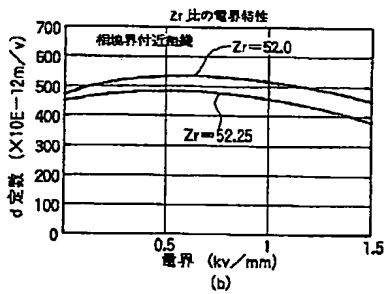
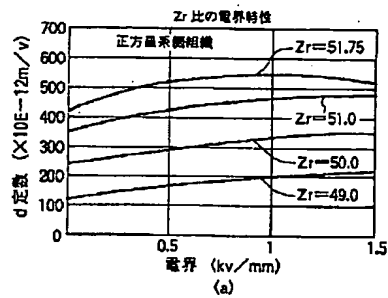
【図1】



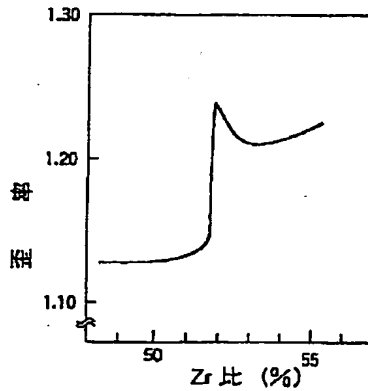
【図2】



【図3】



【図4】



【図5】

